

IN THE SPECIFICATION

Kindly amend the heading on page 1 prior to paragraph [0002] as follows:

Background Art

Kindly amend the heading on page 2 prior to paragraph [0006] as follows:

~~Disclosure of the Invention~~ Summary

Kindly replace paragraphs [0009] and [0013] with the following replacement paragraphs:

[0009] ~~The present invention has been made to respond to the demand. It is an object of the present invention to~~ We therefore provide a martensitic stainless steel pipe of which a heat-affected zone has high resistance to intergranular stress corrosion cracking.

[0010] ~~In order to solve the above problems, the inventors have~~ We intensively investigated the cause of IGSCC occurring in HAZs of girth-welded martensitic stainless steel pipes. As a result, we found that carbides dispersed in a matrix are dissolved into matrix during a welding thermal cycle and Cr carbide precipitates at prior-austenite grain boundaries during following welding thermal cycles to cause the formation of Cr depleted zones around the prior-austenite grain boundaries; hence, IGSCC occurs.

[0011] It is known that stress corrosion cracking caused by such a mechanism occurs in austenitic stainless steel, but it is not presumed that the cracking occurs in martensitic stainless steel. The Cr depleted zones were considered not to be formed in the martensitic stainless steel since the diffusion rate of Cr in a martensitic microstructure is extremely greater than that in an austenitic microstructure and Cr is therefore constantly supplemented even if Cr carbide is formed. However, ~~the inventors~~ we found that the Cr depleted zones are formed even in the martensitic stainless steel under specific welding conditions and IGSCC occurs in a mild corrosion environment.

[0012] ~~The inventors~~ We further found that it is critical to prevent Cr carbide from being formed at prior-austenite grain boundaries in order to prevent IGSCC and the effective content

C_{sol} of dissolved carbon that affects the formation of Cr carbide must therefore be reduced to less than about 0.0050% by mass in such a manner that the C content is extremely reduced or the content of a carbide-forming element, such as Ti, Nb, V, or Zr, having higher ability to precipitate carbides than that of Cr is increased.

[0013] ~~The present invention has been completed based on the above findings and further investigation. The scope of the present~~ Thus, selected aspects of the invention is as follows include:

(1) A martensitic stainless steel pipe having a heat-affected zone with high resistance to intergranular stress corrosion cracking and contains less than about 0.0100% of C; less than about 0.0100% of N; about 10% to about 14% of Cr; and about 3% to about 8% of Ni on a mass basis, wherein the content C_{sol} defined by the following equation (1) is equal to less than 0.0050%:

$$C_{sol} = C - 1/3 \times C_{pre} \quad (1)$$

where $C_{pre} = 12.0 \{Ti/47.9 + 1/2 (Nb/92.9 + Zr/91.2) + 1/3 (V/50.9 + Hf/178.5 + Ta/180.9) - N/14.0\}$ or $C_{pre} = 0$ when $C_{pre} < 0$, where C represents the carbon content, the definition of C_{pre} appears later in equation (2), Ti represents the titanium content, Nb represents the niobium content, Zr represents the zirconium content, V represents the vanadium content, Hf represents the hafnium content, Ta represents the tantalum content, and N represents the nitrogen content on a mass basis.

(2) The martensitic stainless steel pipe specified in Item (1) further contains less than about 0.0100% of C; less than about 0.0100% of N; about 10% to about 14% of Cr; about 3% to about 8% of Ni; ~~Si: about 0.05% to about 1.0% of Si or less; Mn: about 0.1% to about 2.0% of Mn or less; about 0.3% or less of P; about 0.010% or less of S; Al: about 0.001% to about 0.10% or less of Al;~~ one or more selected from the group consisting of about 4% or less of Cu, about 4% or less of Co, about 4% or less of Mo, and about 4% or less of W; and one or more selected from the group consisting of about 0.15% or less of Ti, about 0.10% or less of Nb, about 0.10% or less of V, about 0.10% or less of Zr, about 0.20% or less of Hf, and about 0.20% or less of Ta on a

mass basis, the remainder being Fe and unavoidable impurities, wherein the content C_{sol} defined by equation (1) is equal to less than 0.0050%.

(3) The martensitic stainless steel pipe specified in Item (2) further contains one or more selected from the group consisting of about 0.010% or less of Ca, about 0.010% or less of Mg, about 0.010% or less of REM, and about 0.010% or less of B on a mass basis.

(4) The martensitic stainless steel pipe specified in Item (1) further contains less than about 0.0100% of C; less than about 0.0100% of N; about 10% to about 14% of Cr; about 3% to about 8% of Ni; about 0.05% to about 1.0% of Si; about 0.1% to about 2.0% of Mn; about 0.03% or less of P; about 0.010% or less of S; about 0.001% to about 0.10% of Al; about 0.02% to about 0.10% of V; about 0.0005% to about 0.010% of Ca; and one or more selected from the group consisting of about 4% or less of Cu, about 4% or less of Co, about 4% or less of Mo, and about 4% or less of W on a mass basis, the remainder being Fe and unavoidable impurities, wherein the content C_{sol} defined by equation (1) is equal to less than 0.0050%.

(5) The martensitic stainless steel pipe specified in Item (4) further contains one or more selected from the group consisting of about 0.15% or less of Ti, about 0.10% or less of Nb, about 0.10% or less of Zr, about 0.20% or less of Hf, and about 0.20% or less of Ta on a mass basis.

(6) The martensitic stainless steel pipe specified in any one of Items (1) to (5) is suitable for line pipe uses.

(7) A welded structure comprising the martensitic stainless steel pipe specified in any one of Items (1) to (6), the pipe being welded to a member.

Kindly replace paragraphs [0016] to [0019] with the following replacement paragraphs:

~~Best Mode for Carrying Out the Invention~~ Detailed Description

[0016] ~~The reason for limiting the~~ The composition of a steel pipe of the present ~~invention pipes~~ will now be described. In the description below, the composition is simply expressed in % instead of % by mass.

Less Than 0.0100% C

[0017] Although C is an element that forms a solution in steel and enhances the strength of the steel, a large increase in the C content causes an increase in the hardness of HAZs, an occurrence of welding cracks, and/or a deterioration in the toughness of such HAZs. Therefore, ~~in the present invention,~~ the C content is preferably low. In the present invention, in order to prevent IGSCC from occurring in the HAZs, the C content is limited to less than 0.0100% because C forms Cr carbide, which precipitates to create Cr depleted zones. When the C content is 0.0100% or more, IGSCC can hardly be prevented from occurring in the HAZs. The C content is preferably less than 0.0050%.

[0018] ~~In the present invention, the~~ The C content is limited to the above range and the content of other elements are adjusted such that the effective content C_{sol} of dissolved carbon is reduced to less than 0.0050%. This prevents the Cr depleted zones from being formed, whereby IGSCC can be substantially prevented from occurring in the HAZs. The term "IGSCC can be substantially prevented" means that IGSCC does not occur in welded joints placed in an ordinary environment (for example, an environment with a CO_2 partial pressure of 0.1 MPa, a liquid temperature of 100°C, and a 5% NaCl aqueous solution with a pH of 4.0) in which welded line pipes are usually used, the joints being welded under usual conditions (for example, TIG welding performed with a heat input of 10 kJ/cm).

[0019] The effective content of dissolved carbon C_{sol} is represented by the following equation (1):

$$C_{sol} = C - 1/3 \times C_{pre} \quad (1)$$

The term "effective content of dissolved carbon C_{sol} " means the amount of C that forms Cr carbide that precipitates to create Cr depleted zones during welding. The C_{sol} is determined by subtracting the content of C that bonds to a carbide-forming element such as Ti, Nb, Zr, V, Hf, or Ta from the total C content. That is, the effective content of dissolved carbon C_{sol} is determined by subtracting the content of C that is not consumed in the formation of Cr carbide from the total C content. The content C_{pre} is represented by the following equation (2):

$$C_{pre} = 12.0 \{Ti/47.9 + 1/2 (Nb/92.9 + Zr/91.2) + 1/3 (V/50.9 + Hf/178.5 + Ta/180.9) - N/14.0\} \quad (2)$$

wherein C represents the carbon content, Ti represents the titanium content, Nb represents the niobium content, Zr represents the zirconium content, V represents the vanadium content, Hf represents the hafnium content, Ta represents the tantalum content, and N represents the nitrogen content in percent by mass and $C_{pre} = 0$ when $C_{pre} < 0$. When the content C_{pre} is calculated, the content of uncontained one among the elements used in equation (2) is zero. These elements have different abilities to form carbide and different abilities to dissolve carbide. Therefore, in the equation to determine the content C_{pre} used herein, the abilities of Nb and Zr are estimated to be one half of the ability of Ti and the abilities of V, Hf, and Ta are estimated to be one third of the ability of Ti based on experiment results. Since the steel pipe ~~of the present invention~~ contains N, the following elements primarily form nitrides: Ti, Nb, Zr, V, Hf, and Ta. Therefore, in the equation to determine the content C_{pre} used herein, the content of N that forms nitrides together with Ti, Nb, Zr, V, Hf, and Ta is subtracted from the total N content. In consideration that the Cr depleted zones are formed in the HAZs, that is, the HAZs are in a nonequilibrium state, the content of C that forms carbides other than Cr carbide to prevent the formation of Cr carbide is estimated to be one third of the content C_{pre} .

Kindly replace paragraphs [0021] and [0022] with the following replacement paragraphs:

[0021] N, as well as C, is an element that forms a solution in steel and enhances the steel strength. A large increase in the N content causes an increase in the hardness of the HAZs, an occurrence of welding cracks, and/or a deterioration in the toughness of the HAZs. Therefore, ~~in the present invention~~, the content of N is preferably low. N bonds to Ti, Nb, Zr, V, Hf, and Ta to form nitrides. This leads to the reduction in the content of Ti, Nb, Zr, V, Hf, and Ta that can form carbides to prevent the formation of Cr carbide and also leads to the deterioration in ability to prevent IGSCC by preventing the formation of the Cr depleted zones. Therefore, the N content is preferably low. Since the negative effects of N are negligible when the N content is less than 0.0100%, the N content is herein limited to less than 0.0100%. The N content is preferably 0.0070% or less.

10% to 14% Cr

[0022] Cr is a basic element for enhancing corrosion resistances such as CO₂ corrosion resistance, pitting resistance, and resistant to sulfide stress cracking. ~~In the present invention, the~~ The Cr content must be 10% or more. However, when the Cr content is more than 14%, the ferrite phase is likely to be formed suppressing formation of martensitic microstructure. Therefore, in order to form a martensitic microstructure with high reproducibility, a large amount of an alloy element must be used. This causes an increase in material cost. Thus, ~~in the present invention,~~ the Cr content is limited to the range of 10% to 14%.

Kindly replace paragraphs [0025] and [0026] with the following replacement paragraphs:

0.05% to 1.0% Si

[0025] Si is an element that functions as a deoxidizing agent and enhance solid solution hardening. ~~In the present invention, the~~ The Si content is may be 0.05% or more. However, when the Si content is more than 1.0%, the toughness of a base metal material and the toughness of the HAZs are low because Si is an element for forming ferrite. Therefore, the Si content is preferably limited to the range of 0.05% to 1.0%. The Si content is more preferably 0.1% to 0.5%.

0.1% to 2.0% Mn

[0026] Mn is an element that increases solid solution hardening, forms austenite, and prevents the formation of ferrite to enhance the toughness of the base metal material and that of the HAZs. In order to achieve such advantages, ~~in the present invention,~~ the Mn content is preferably 0.1% or more. However, when the Mn content is more than 2.0%, the effect thereof is saturated. Therefore, the Mn content is limited to the range of 0.1% to 2.0%. The Mn content is more preferably 0.2% to 1.2%.

Kindly replace paragraph [0028] with the following replacement paragraph:

0.010% or less S

[0028] S is an element that forms a sulfide such as MnS to cause a deterioration in machinability. ~~In the present invention, the~~ The S content is preferably low. The allowance of the S content is 0.010% or less. Therefore, the S content is preferably limited to 0.010% or less. Since an excessive decrease in the S content causes a large increase in refining cost and a decrease in productivity, the S content is preferably 0.0005% or more.

Kindly replace paragraph [0030] with the following replacement paragraph:

One or more selected from the group consisting of 4% or less Cu, 4% or less Co, 4% or less Mo, and 4% or less W

[0030] Cu, Co, Mo, and W are elements for enhancing CO₂ corrosion resistance that is one of properties necessary for steel pipes for pipelines for transporting natural gas containing CO₂. The steel pipe ~~of the present invention~~ contains one or more selected from those components in addition to Cr and Ni.

Kindly replace paragraph [0038] with the following replacement paragraph:

One or more selected from the group consisting of 0.010% or less Ca, 0.010% or less Mg, 0.010% or less REM, and 0.010% or less B

[0038] Ca, Mg, REM, and B are elements for enhancing the hot workability and the productivity of continuous casting processes. The steel pipe may contain at least one selected from those elements according to needs. In order to achieve such advantages, it is preferable that the Ca content be 0.0005% or more, the Mg content be 0.0010% or more, the REM content be 0.0010% or more, or the B content be 0.0005% or more. However, when the Ca content is more than 0.010%, the Mg content is more than 0.010%, the REM content is more than 0.010%, or the B content is more than 0.010%, those components are likely to form coarse inclusions to cause a serious deterioration in corrosion resistance and toughness. Therefore, it is preferable that the Ca content be limited to 0.010% or less, the Mg content be limited to 0.010% or less, the REM

content be limited to 0.010% or less, or the B content be limited to 0.010% or less. Ca is useful in stabilizing the quality of the steel pipe and useful in reducing manufacturing cost. That is, Ca is preferable in quality stability and cost efficiency. The Ca content is more preferably within the range of ~~0.005%~~ 0.0005% to 0.0030%.

Kindly replace paragraph [0040] with the following replacement paragraph:

[0040] A preferable method for manufacturing the steel ~~pipe of the present invention~~ pipes will now be described using a seamless steel pipe as an example.

Kindly replace paragraphs [0043] and [0044] with the following replacement paragraphs:

[0043] The steel ~~pipe of the present invention is~~ pipes are not limited to the type of seamless steel pipe described above. The steel pipe material with the above composition may be processed into a welded steel pipe such as an electric resistance welded pipe, a UOE steel pipe, or a spiral steel pipe by an ordinary procedure.

[0044] The martensitic stainless steel pipe ~~of the present invention~~ is useful in manufacturing a welded structure by welding. Examples of the welded structure include oil or natural gas production facilities such as pipelines manufactured by girth-welding line pipes, chemical plant pipes such as risers and manifolds, and bridges. The welded structure specified herein may be manufactured by welding the martensitic stainless steel pipes of the present invention, welding the martensitic stainless steel pipe of the present invention to another type of steel pipe, or welding the martensitic stainless steel pipe ~~of the present invention~~ to a member made of another material.

Kindly replace paragraphs [0055] and [0056] with the following replacement paragraphs:

[0055] All the test pieces of examples ~~of the present invention~~ are superior in resistance to intergranular stress corrosion cracking that is likely to occur in HAZs because IGSCC is prevented from occurring in the HAZs without subjecting the test pieces to post-welding heat treatment. The steel pipes of the examples have high strength, toughness, CO₂ corrosion resistance, and resistant to sulfide stress cracking which are necessary for line pipes. The No. 20

steel pipe (an example ~~of the present invention~~) suffers from pitting in the carbon dioxide corrosion test and cracking in the sulfide stress corrosion cracking test because the steel pipe has a Mo content that is outside the more preferable range ~~of the present invention~~. However, this steel pipe does not suffer cracking in the U-bend test for evaluating resistance to stress corrosion cracking. Thus, no problem will arise if a steel pipe with a Mo content that is slightly outside the more preferable range ~~of the present invention~~ is used as a line pipe as long as the line pipe need not have high CO₂ corrosion resistance, and resistant to sulfide stress cracking. In contrast, the steel pipes of comparative examples ~~that are outside the scope of the present invention~~ suffer from IGSCC which occurs in HAZs thereof, that is, the HAZs have an insufficient resistance to intergranular stress corrosion cracking.

Industrial Applicability

[0056] ~~The present invention provides an~~ We provide inexpensive martensitic stainless steel pipe pipes having high strength, toughness, CO₂ corrosion resistance, resistance to stress corrosion cracking, and resistance to intergranular stress corrosion cracking. The martensitic stainless steel pipe is suitable for a base metal material for line pipes. In the martensitic stainless steel pipe, IGSCC can be prevented from occurring in a HAZ and needs not post-welding heat treatment. That is, the martensitic stainless steel pipe is industrially advantageous in particular. The martensitic stainless steel pipe of the present invention has high hot workability, hardly has surface defects, and is superior in productivity.